In-situ LA-ICP-MS analysis of a colloform-banded veinlet from the epithermal Au-Ag Khan Krum deposit, SE Bulgaria

In-situ изследване с LA-ICP-MS на коломорфно-ивичеста жилка от епитермалното Ag-Au находище Хан Крум, ЮИ България

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Introduction

The colloform-banded veins in Khan Krum deposit (also known as Ada Tepe deposit) point to the economic portion of the deposit and appear in centimeter- and milimeter scales as bonanza electrum grades are identified only in millimeter- to sub-millimeter-wide veinlets. In order to answer the question about their different electrum grade we analyzed a colloform-banded veinlet containing several electrum-poor macro-bands and one electrum-rich submillimeter-wide banding.

Material and methods

The studied hand specimen of colloform-banded texture is obtained from a high-angle veinlet about 2.5 cm wide, which crops out on the summit of the Ada Tepe ridge. The major, minor and trace element abundances of the veinlet are determined on a polished section by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) measurements. The quantities of silicon (as major element in the sample) in assigned particular areas are preliminary determined by electron microprobe analysis (EPMA), and accepted as internal element standard values for the LA-ICP-MS calculations. The final element compositions are obtained by data reduction software Iolite. We determined the abundances of 23 chemical elements and their isotopes in each macro- and micro-band as follows: ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{42}Ca, ^{49}Ti, ^{53}Cr, ^{57}Fe, ^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{95}Mo, ^{107}Ag, ^{121}Sb, ^{125}Te, ^{137}Ba, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U.

The analytical procedure with LA-ICP-MS included measurements of each macro-band in one or two spots (spot diameter 35 μm), ablating three craters near each spot, staying away from any opaque mineral. Bands consist of quartz and adularia of varying ratio, of electrum of different grade, and of pyrite of varying abundance. No any other minerals are observed under optical microscope, which highest magnification is 200×. Generally, the macro-bands contain micron-sized electrum of low grade and scarce pyrite, while the micro-banding contains electrum of moderate to high grades, and pyrite of moderate to high abundances. None of these electrum types is macroscopically visible. The micro-banding consists of four micro-bands (numbered 8a, 8b, 8c, and 8d) as dense electrum aggregates and abundant pyrite are present only in the micro-band 8d (formed nearest to the footwall). Each micro-band is ablated in three near-by craters around a transverse imaginary line.

Results and discussion

Considering all spots analyzed, there is high positive linear correlation (R) between Al and K (R=0.92), on one side, and high negative linear correlation between Al and Si (R=–0.94), and between K and Si (R=–0.96), on the other side, which means that nearly all K and Al are bound in potassium feldspar (adularia), thus confirming the previous petrographical and powder X-Ray diffraction data. It is worth to say that because of the irregular distribution of adularia and quartz within the bands, and the large operating area of the LA-ICP-MS analysis (spot diameter 35 μm) compared to the size of mineral grains (below 10 μm) it is not possible to evaluate properly the relationship between potassium and gold, revealed already with the petrographical observations as positive correlation between adularia and electrum abundances. Nevertheless, the correlation between K, and respectively Al, and other chemical elements display some interesting relationships. The abundances of K and Al are highest (about 10 times and more) in two macro-bands and in all micro-bands. However, the abundances of Au, Fe, Cu, Zn, As, Te, Pb, and Bi are 10 and more times higher only in the micro-band 8d, where electrum appears in highest grade compared to the other micro-bands and the macro-bands. This means, that the very high adularia abundance is necessary (inferring extreme degree of boiling of fluids), but not enough premise for bonanza electrum ores. Further, considerable difference between the macro- and the micro-bands appear when we consider the abundances of Bi, Te, Cu, Pb, Zn, Au, and Ba. Their highest abundances are determined in the four micro-bands. This difference can be best expressed by the ratio of the average abundance of a given element in the macro-bands to this one in the micro-banding. The micro-banding is enriched in the following elements (in times, in decreasing order): Bi (63), Te (39), Cu (36), Fe (33), Pb (29), Au (18), As (18), U (7), Ba (5), Zn (4), Mg (4), Cr (3), Al (2), Tl (1.6), Na (1.5), K (1.4), and Th (1.2), and is slightly depleted in the following elements: Si (0.9), Ti (0.8), Se (0.8), Ag (0.8), and Sb (0.5). Ca has equal abundances in both macro- and micro-bands. This coefficient of enrichment is even more pronounced when we consider ratios of element abundances in the macro-bands as a whole to these ones in the micro-band 8d. The high abundances of Bi, Te, Cu, Fe, Pb, Au, As, and Zn in the micro-banding are most likely related to mineral phases some of which have been reported from optical observations and EMPA: hessite (Ag_2Te), petzite (Ag_3AuTe_2), galena (Marchev et al., 2004), pyrite, marcasite, chalcopyrite, arsenopyrite, sphalerite, electrum (Kunov et al., 2001; Marchev et al., 2004. It is important to underline here that the high-grade electrum associates with sulfides, and Au-Ag and Ag tellurides because this fact infers the following: (i) the deposition of gold and silver was very sensitive to the decrease in the activities of reduced sulfur and tellurium species; (ii) the transportation of gold and silver in the paleofluids was in the form of complexes with sulphur, and tellurium, and (iii) the high sulphur and tellurium abundances appeared to be critical parameters for high gold grades, as the higher sulphur, and tellurium, the higher the gold in the ores under equal other conditions.

For mineral-genetic speculations, it is important to mention the Se/Te ratio in the colloform-banded veinlet analyzed. In the macro-bands the average Se/Te ratio is 0.94 (or Se≈Te), while in the bonanza micro-banding this ratio is 0.02 (or Te>>Se), i.e. the bonanza veins in Khan Krum deposit are Te-rich and Se-poor, a feature indicating mafic igneous source (Shikazono et al., 1990; Koneev et al., 2006; Saunders and Bruseke, 2012). Such a mafic source has been suggested by Marchev et al. (2006) on the basis of petrographical and isotopic data. Another important ratio, Au/Ag, also displays different values in the macro- and micro-bands. The average Au/Ag ratio in the macro-bands is 0.08, while in the micro-banding is 1.87. In particular, the Au/Ag ratio for the 8a, 8b, and 8c micro-bands is similar: 0.2, 0.2, and 0.9, respectively, while this ratio in micro-band 8d is quite higher: 7.5.

The LA-ICP-MS data appear compositional evidence that the micro-banding is formed from an individual hydrothermal pulse highly enriched in Au, Fe, As, Te, Pb, Cu, and Bi (and by inference in S) and/or through very effective mechanism of deposition of these metals compared to the individual macro-bands. The enrichment of the micro-band 8d in Au, Fe, As, Te, Pb, Cu, and Bi compared to the other micro-bands can be reasonably explain with the deposition of 8d from another hydrothermal pulse highly enriched in the mentioned above chemical elements. The similar width of micro-bands 8a, 8b, and 8c (0.03, 0.03, 0.06 mm, respectively) versus the quite larger width of micro-band 8d (0.20 mm) combined with its very distinctive Au/Ag ratio, support this idea.

Conclusions

1. The Khan Krum deposit is Au- (Au>Ag) and Te-rich (Te>Se) type epithermal deposit, thus indicating its relationship to a deep mafic magma; **2.** The micro-banding compared to the macro-bands is enriched in Bi, Te, Cu, Fe, Pb, Au, As, U, Ba, Zn, Mg, Cr, Al, Tl, Na, K, and Th; and it is slightly depleted in Si, Ti, Se, Ag, and Sb; Ca has equal abundances in both macro- and micro-bands; **3.** The highest grades of electrum are linked with the highest abundances of Fe, As, Cu, Pb, Zn, Bi, and Te which deposited as sulfides and tellurides reveal the deposition of economic gold in response to the decrease of activities of S and Te in the paleofluids; **4.** It seems that most critical premises for high electrum grades under equal other conditions are the extreme degree of boiling, and the high abundances of sulfur, and of tellurium in the fluids.

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